On the Catalytic Decomposition of Oxalic Acid by Colloidal Platinum.

By **Isamu SANO.**

(Received March 28, 1940).

It is well known, as an established fact for a long time, that oxalic acid is appreciably decomposed in its aqueous solutions by a variety of agents such as light,(1) moulds(2) as well as metals in finely divided state.(3)

In the last communication,(4) the present writer made a description of the results obtained in the decomposition of the acid due to oxidation with the air, which is catalyzed by the colloidal platinum-carbonyl as well as by the colloidal platinum obtainable by leaving it alone in contact with the air. The sols of platinum-carbonyl tinged with red as well as of platinum tinged with black, were both used without subjected to dialysis, and therefore, they were contaminated with hydrochloric acid liberated from chloroplatinic acid through the reducing action of carbon monoxide, although the acid is likely to have little influence upon the stability of the sols thus produced.(5)

The red sols of platinum-carbonyl may be easily obtained, as already reported,(4) by passing carbon monoxide through dilute aqueous solutions of chloroplatinic acid for some time at ordinary temperature. By dialyzing the red sol, it turns black in due time to convert into a sol of platinum.(5)

The present communication deals with the experiments on the decomposition of oxalic acid catalyzed by the black sol of platinum obtained by means of dialysis of the red one.

Experimental. A 0.05% aqueous solution of chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) was used in preparing the red sol in each run of the experiments. Carbon monoxide was produced by heating the mixture of formic acid instead of oxalic acid previously used and concentrated sulphuric acid, and then, purified by passing through alkaline hydroxide solutions. The passage of carbon monoxide through the acid solutions was done at nearly a constant rate of 3 litres per hour throughout the

---

(1) P. Carles, *Compt. rend.*, **71** (1870), 226; G. Bizio, *Z. anal. Chem.*, **9** (1870), 392; A. Downes and T. P. Blunt, *Proc. Roy. Soc.* (London), **29** (1879), 219; E. Duclaux, *Compt. rend.*, **103** (1886), 1011; K. Wehmer, *Botan. Ztg.*, **1891**, 49; *Chem. Zentr.*, **62** (1891), II, 476; **63** (1892), I, 171; T. Gigli, *Chem. Zentr.*, **64** (1893), I, 11; A. Richardson, *J. Chem. Soc.*, **65** (1894), 450; H. de Vries, *Z. angew. Chem.*, **1899**, 521; W. P. Jorissen, *Z. angew. Chem.*, **1899**, 521; S. Ishimaru, *J. Chem. Soc. Japan*, **43** (1922), 767; **53** (1932), 449; *Science Repts. Tohoku Imp. Univ.*; Ser. I, **24** (1935), 411.

(2) C. Neubauer, *Z. anal. Chem.*, **9** (1870), 392; W. N. Hartley, *Chem. News*, **37** (1878), 9; G. Fleury, *Chem. Zentr.*, **14** (1883), 547; O. Warburg, *Untersuch. botan. Inst. Tübingen*, **2** (1886-8), 117; K. Wehmer, *Botan. Ztg.*, **1891**, 49; *Chem. Zentr.*, **62** (1891), II, 476; **63** (1892), I, 171; W. P. Jorissen, *Z. angew. Chem.*, **1899**, 521.

(3) O. Šulc, *Z. physik. Chem.*, **28** (1899), 719.

(4) I. Sano, this Bulletin, **14** (1939), 121.

(5) I. Sano, this Bulletin, **9** (1934), 320.

experiments. The red sol was dialyzed, immediately after its formation, with parchment paper for a few days with the frequent renewal of dialysate until freed from chlorine ions. Care was taken to keep the volume of the sol constant through the course of dialysis, this being conducted in a flanged glass-tube with graduation, open at both ends, over the bottom of which the membrane was tightly tied with a cord. Consequently, the black sol of platinum thus obtained might be reasonably inferred from calculation to contain 0.188 grams of platinum in one litre, the same as in the red sol of platinum-carbonyl so far as the content of platinum is concerned. It must be mentioned for reference that the sol was exposed, by way of precaution, to the action of ultrasonics for a few minutes prior to use in order to make sure of its dispersion, since the sol has a slight tendency, particularly if concentrated,(6) to settle to some extent.

The reactions were carried out at 50.0°C. under diffused day-light. The procedures were the same as in the last communication.(4) The reacting mixtures consisting of 10 c.c. of aqueous solution of oxalic acid of a definite concentration and 2 c.c. of the black sol were placed in test-tubes provided with a rubber stopper through which a capillary glass-tube was inserted as a line of communication of the air, and enough agitated at short intervals during the course of the run. The acid contents of the test-tubes were, by turns, titrated with a 0.1 N barium hydroxide solution at the desired intervals of time.

Results and Discussion. The results are given in Tables 1, 2, 3, 4 and 5, where t represents the time elapsed from the start in hours, c the titre of the reacting solution titrated with the barium hydroxide solution at time t in c.c. The meanings of c_k and t_k in the tables will be elucidated later.

With the intention of verifying the condition indispensable for the progress of the reaction accelerated through the existence of colloidal platinum that the reacting solution must be charged with dissolved oxygen, a number of runs were made at 50.0°C. in test-tubes hermetically sealed. The results are shown in Tables 6 and 7.

Table 1. Concentration of oxalic acid solution: 0.10 N

t	c	c_k ($t_k = 1$)
0	11.32 (c_0)	—
1	11.04	11.04
3	10.85	11.03
5	10.62	10.98
7	10.46	11.00
9	10.28	11.00
11	10.06	10.96
13	10.00	11.07
16	9.82	11.16
19	9.42	11.03
23	9.08	11.05
27	8.51	(10.84)
31	8.06	(10.75)

These results were plotted on a graph with the values of $c_0 - c$ as ordinates and of t as abscissæ in Fig. 1, 2, 3 and 4, where the figure attending on the curve states the number of the table referred to. If the reaction catalyzed by colloidal platinum should, in process of time, pass to proceed in conformity to the formula for a reaction of zero order

$$-dc/dt = k \quad \text{or} \quad c_0 - c = kt,$$

---

(6) I. Sano, this Bulletin, **15** (1940), 106.

Table 2. Concentration of oxalic acid solution: 0.10 N

t	c	c_k ($t_k = 4$)
0	11.28 (c_0)	—
2	10.88	—
4	10.51	10.51
6	10.28	10.47
8	10.15	10.53
10	9.96	10.53
12	9.74	10.51
15	9.49	10.54
20	8.97	10.50
24	8.58	10.49
27	8.17	(10.37)
31	7.57	(10.15)

Table 3. Concentration of oxalic acid solution: 0.05 N

t	c	c_k ($t_k = 1$)
0	5.72 (c_0)	—
1	5.46	5.46
3	5.26	5.44
5	5.08	5.43
7	4.91	5.44
9	4.74	5.46
12	4.56	5.53
15	4.20	5.44
20	3.76	5.44
24	3.40	5.43
27	3.24	5.54
30	2.87	5.43
32	2.52	(5.26)

Table 4. Concentration of oxalic acid solution: 0.025 N

t	c	c_k ($t_k = 1$)
0	3.03 (c_0)	—
1	2.82	2.82
3	2.64	2.80
5	2.45	2.78
7	2.34	2.83
9	2.02	2.67
12	1.92	2.82
15	1.57	2.72
19	1.42	2.89
22	1.16	2.88
25	0.79	2.73
28	0.69	2.90
32	0.30	2.84

Table 5. Concentration of oxalic acid solution: 0.025 N

t	c	c_k ($t_k = 2$)
0	3.02 (c_0)	—
1	2.81	—
3	2.50	2.59
4	2.38	2.56
6	2.27	2.63
10	1.91	2.62
12	1.68	2.57
16	1.34	2.58
20	1.06	2.66
24	0.51	2.47
28	0.27	2.58
32	0.19	(2.86)

Table 6. Concentration of oxalic acid solution: 0.10 N

t	c	c_k($t_k = 1$)
0	11.30 (c_0)	—
1	10.96	10.96
2	10.86	10.93
3	10.78	10.92
6	10.60	10.96
9	10.34	10.92
12	10.19	10.98
15	9.90	10.61
21	9.88	—
24	9.85	—
27	9.82	—
30	9.76	—

Table 7. Concentration of oxalic acid solution: 0.025 N

t	c	c_k ($t_k = 1$)
0	3.10 (c_0)	—
1	2.67	2.67
3	2.60	2.75
6	2.24	2.62
9	2.06	2.67
12	1.86	—
15	1.78	—
18	1.62	—
21	1.58	—
24	1.50	—
27	1.45	—
30	1.28	—

where c_0 is the original concentration of the reacting solution and k the velocity constant, there should exist a portion of straight line in the curve representing the relation between $c_0 - c$ and t, and this is the actual case as shown in Fig. 1, 2 and 3. The reaction takes place immediately after the addition to the acid solution of the black sol dialyzed beforehand and proceeds smoothly, this forming a contrast to the progress of the reaction catalyzed by the red sol in which case there can be distinctly seen an induction period at the outset.(4) Although the incipient part of Curves 1, 2, 3, 4 and 5 in the figures changes its course in a short time after the

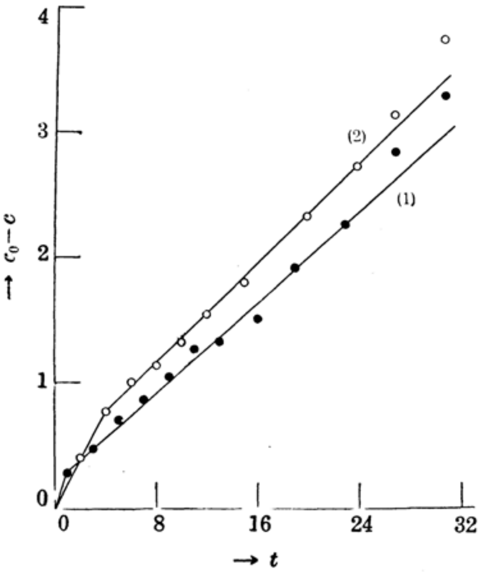

Fig. 1.

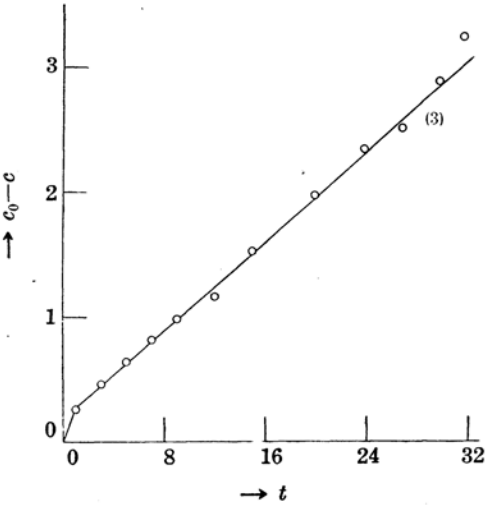

Fig. 2.

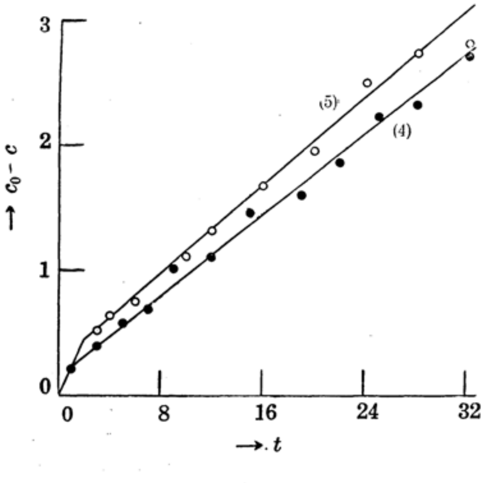

Fig. 3.

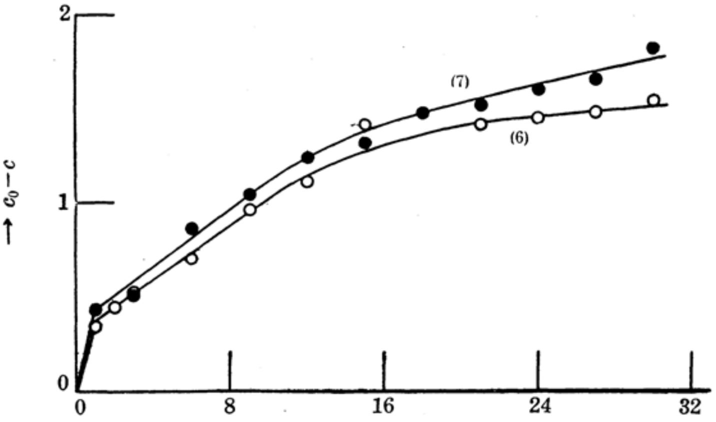

Fig. 4.

commencement of reaction, the subsequent part of it assumes a rectilinear figure within the range of measurement performed. The turning-point in the curve following on the heels of the transition period might make its appearance, as described in the last communication,(4) in consequence of the coagulation of the sol by electrolyte and, in particular, by heat. The catalyzing ability of colloidal particle must be reduced to some extent through coagulation in the course of the transition period. It may be supposed for the coagulation to occur the more promptly and strongly, the more concentrated the oxalic acid solution and the higher the temperature of reaction is. It was observed as a matter of fact that in dilute solutions of the acid, the sol was apparently stable throughout one run of the experiments; while in concentrated solutions, it somewhat flocculated in due course of time to have a slight tendency to settle at the bottom. The magnitudes of the velocity constant corresponding for the linear portion of curve in the figures were found, however, to be approximately identical with one another as in the table shown below, this being in striking contrast to the results obtained with the sols not subjected to dialysis in advance, according to which it was very likely for the reactions to proceed in accordance with the formula for the type of first order, and moreover, it was undeniable for the velocity constant to be notably affected by the concentration of the acid solution. In the cases of the reactions with the sols dialyzed, it is found for them, as indicated above, to be rather of the type of zero order. The applicabilities of the alternative types can be clearly seen particularly with dilute solutions of the acid.

Number of table	Concentration of aqueous solution of oxalic acid (N)	$k=(c_0-c)/t$
1	0.10	0.0895
2	0.10	0.0957
3	0.05	0.0883
4	0.025	0.0818
5	0.025	0.0889
6	0.10	0.0720
7	0.025	0.0767

This remarkable difference may be attributed to the singularity of conditions of the surface of colloidal particle due to dialysis by dint of which the sol could be set free from contamination by electrolyte. It might be supposed for the colloidal particles to be invested with the enhanced adsorptive as well as catalytic ability through the process of dialysis, and in consequence, to be capable of adsorbing the reactant strongly and extensively; this implies that the available surface of particle may be practically saturated with reactant at the concentrations prevailing and the reaction velocity independent of concentration, the reaction being therefore of zero order. It can be definitely seen, however, that Curves 1, 2 and 3 are only approximately linear to go on increasing with the lapse of time, although Curves 4 and 5 are both of rectilinear figure throughout the course of reaction concerned.

The value of c_k tabulated previously was computed from k shown above in conformity to the formula for reaction of zero order

$$c_k - c = kt,$$

where c signifies the titre of oxalic acid solution as before at time t reckoned from a virtual starting-point of estimation denoted by t_k in the tables. It can be anticipated for c_k to take a constant value in each run of the experiments if the reaction concerned should be of zero order.

Taking these circumstances into account, some theoretical discussion of the subject will be made below. If θ_1 is the fraction of the available surface covered unimolecularly with molecules of oxalic acid and θ_2 with molecules of oxygen at any time, it will follow under the same assumptions as in the last communication⁽⁴⁾ that for equilibrium between the adsorbed layer consisting of both molecules of oxalic acid as well as oxygen and those in the surrounding medium

$$a_1 \mu_1 (1-\theta_1-\theta_2) = \nu_1 \theta_1 \quad \text{and} \quad a_2 \mu_2 (1-\theta_1-\theta_2) = \nu_2 \theta_2 ,$$

a_1 and a_2 being the fraction of the numbers of molecules of oxalic acid and oxygen, μ_1 and μ_2, colliding with the surface of colloidal catalyst in unit time which remain, and $\nu_1\theta_1$ and $\nu_2\theta_2$ the numbers of molecules of oxalic acid and oxygen which leave the surface in unit time. The presence of molecules of water as solvent may be set at naught because of the hydrophobic nature of the colloidal particle involved.

Neglecting θ_2 in comparison with θ_1 under the assumption that the surface is covered only sparsely with molecules of oxygen, though to a much greater extent with molecules of oxalic acid, so that $\theta_2 \ll \theta_1 < 1$, it follows that

$$a_1 \mu_1 (1-\theta_1) = \nu_1 \theta_1 \quad \text{and} \quad a_2 \mu_2 (1-\theta_1) = \nu_2 \theta_2 .$$

Solving these for θ_1 and θ_2,

$$\theta_1 = a_1 \mu_1 / (a_1 \mu_1 + \nu_1) \quad \text{and} \quad \theta_2 = \nu_1 a_2 \mu_2 / \nu_2 (a_1 \mu_1 + \nu_1) .$$

Since it may be presumed for the rate of reaction, v, referred to the oxalic acid concentration, c, to be proportional to the amounts of reactants adsorbed on the available surface, it will be given by

$$v = k \theta_1 \theta_2 ,$$

k being the velocity constant. This points to the rate-determining process suggested in the last communication(4)

$$C_2O_4H_2 + O_2 = 2\,CO_2 + H_2O_2.$$

Substituting θ_1 and θ_2 obtained from the above equations, it follows that

$$\begin{aligned} v &= k\left\{a_1\,\mu_1 \,/\, (a_1\,\mu_1+\nu_1)\right\}\cdot\left\{\nu_1\,a_2\,\mu_2 \,/\, \nu_2\,(a_1\,\mu_1+\nu_1)\right\} \\ &= k' a_1\,\mu_1\,\mu_2 \,/\, (a_1\,\mu_1+\nu_1)^2, \end{aligned}$$

where k' is set up of a combination of various constants such as k, ν_1, ν_2 and a_2.

Now, reference must be made to the aspect(7) that there should exist a relationship shown by the formulation

$$Z = n\sqrt{(RT \,/\, 2\pi M)}$$

between the number of molecules of any reactant, Z, striking unit area of the available surface of catalyst from its surrounding medium in unit time and the concentration, c, of the reactant in the medium, where n shows the number of molecules of reactant per c.c., R the gas constant, T the temperature and M the molecular weight of the reactant, this indicating Z to be proportional to c as assumed previously.(4),(8)

Thus, the velocity equation mentioned above may be rewritten in the form

$$-dn \,/\, dt = k' a_1\,s\,\kappa\,n\,\mu_2 \,/\, (a_1\,s\,\kappa\,n+\nu_1)^2,$$

where κ stands for $\sqrt{(RT/2\pi M)}$, n the number of molecules of oxalic acid per c.c. at time t and s the total area of available surface of catalyst. Since μ_2 is presumed to be constant throughout the run of the experiments on account of the reacting system being continually supplied with oxygen from the outside, this reduces to

$$-dn \,/\, dt = k'' a_1\,s\,\kappa\,n \,/\, (a_1\,s\,\kappa\,n+\nu_1)^2,$$

k'' being a constant including μ_2. On integration it follows that

$$(n_0-n)\left\{(a_1\,s\,\kappa \,/\, 2)\cdot(n_0+n)+2\nu_1+(\nu_1^2 \,/\, a_1\,s\,\kappa)\cdot\ln\,(n_0 \,/\, n) \,/\, (n_0-n)\right\} = k''t\,,$$

where n_0 indicates the number of molecules of oxalic acid at the outset of reaction. Putting

$$K(n) = (a_1\,s\,\kappa \,/\, 2)\cdot(n_0+n)+2\nu_1+(\nu_1^2 \,/\, a_1\,s\,\kappa)\cdot\ln\,(n_0 \,/\, n) \,/\, (n_0-n)$$

$$K_1(n) = (a_1\,s\,\kappa \,/\, 2)\cdot(n_0+n) \quad \text{and} \quad K_2(n) = (\nu_1^2 \,/\, a_1\,s\,\kappa)\cdot\ln\,(n_0 \,/\, n) \,/\, (n_0-n)$$

the equation becomes

---

(7) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," 22, Oxford (1933).

(8) I. Sano, this Bulletin, **13** (1938), 118.

$$n_0 - n = (k'' / K(n))\, t\,.$$

This suggests the reaction to be of zero order, if $K(n)$ could be assumed to be constant, since $n_0 - n$ is proportional to $c_0 - c$, and this would be the actual case as is to be anticipated from the following consideration. The functions, $K_1(n)$ and $K_2(n)$, are monotonously increasing and decreasing with increasing n respectively, and accordingly, the function $K(n)$ would assume a roughly constant value over a certain range of varying n. This is schematically indicated in Fig. 5, Curves K_1, K_2 and K speaking for the variation of the functions, $K_1(n)$, $K_2(n)$ and $K(n)$, with n respectively. Considered in this light, the reaction should proceed practically in line with the formula for the type of zero order.

It has been reported already that oxalic acid is decomposed in its aqueous solutions in the presence of oxygen. The effect is definitely shown by Curves 6 and 7 in Fig. 4. In these runs the reaction was performed in test-tubes hermetically sealed in order of keeping out the air from the outside. It can be explicitly seen the drift to occur in the course of time from want of oxygen.

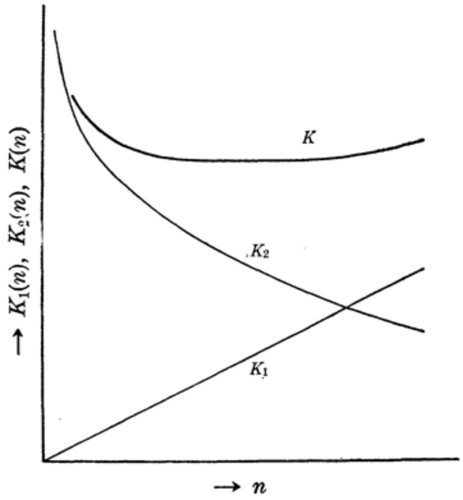

Fig. 5.

From what has been stated, the catalytic decomposition of oxalic acid in its aqueous solutions accelerated by colloidal platinum in the presence of oxygen may be accounted for in the same manner as described in the last communication⁽⁴⁾; that is,

$$C_2O_4H_2 + O_2 = 2\,CO_2 + H_2O_2 \qquad \text{(slow)}$$
$$H_2O_2 = H_2O + O \qquad \text{(rapid)}$$
$$O + C_2O_4H_2 = 2\,CO_2 + H_2O \qquad \text{(rapid)}$$

Therefore, the velocity of the reaction

$$2\,C_2O_4H_2 + O_2 = 4\,CO_2 + 2H_2O$$

should be determined by the first step of decomposition.

Summary.

(1) The decomposition of aqueous solutions of oxalic acid (0.10, 0.05 and 0.025 N) due to oxidation accelerated by colloidal platinum obtained through the process of dialysis of colloidal platinum-carbonyl was investigated, in the presence of oxygen and diffused day-light, during a period extending over thirty hours at 50.0°C.

(2) It appears that the greater part of the course of reaction proceeds in accordance with the formula for the type of zero order after it passed incipiently through a short period of transition and the rate of reaction is scarcely influenced by the concentration of reacting solution.

(3) It was definitely shown that the reaction should be retarded if the supply of oxygen is cut off.

(4) The above results were explained in conformity with the mechanism of reaction previously proposed.

The author wishes to express his cordial thanks to Prof. J. Sameshima under whose kind guidance the present work has been carried out. The expense of it has been defrayed from the Committee on Catalysis in the Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.